3. Industrial Processes

Greenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO_2) , methane (CH_4) , or nitrous oxide (N_2O) . The processes addressed in this chapter include cement production, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use, CO_2 consumption, iron and steel production, ammonia manufacture, ferroalloy production, aluminum production, petrochemical production, silicon carbide production, adipic acid production, and nitric acid production (see Figure 3-1).

Figure 3-1: 1998 Industrial Processes Chapter GHG Sources

In addition to the three greenhouse gases listed above, there are also industrial sources of several classes of manmade fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, they will continue to accumulate in the atmosphere as long as emissions continue. Sulfur hexafluoride, itself, is the most potent greenhouse gas the IPCC has ever evaluated. Usage of these gases, especially HFCs, is growing rapidly as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

In 1998, industrial processes generated emissions of 67.0 MMTCE, or 3.7 percent of total U.S. greenhouse gas emissions. Carbon dioxide emissions from all industrial processes were 18.4 MMTCE (67,447 Gg) in the same year. This amount accounted for only 1 percent of national CO₂ emissions. Methane emissions from petrochemical and silicon carbide production resulted in emissions of approximately 0.4 MMTCE (78 Gg) in 1998, which was less than 1 percent of U.S. CH₄ emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 7.7 MMTCE (91 Gg) in 1998, or 6 percent of total U.S. N₂O emissions. In the same year, combined emissions of HFCs, PFCs and SF₆ totaled 40.5 MMTCE. Overall, emissions from industrial processes increased by 39 percent from 1990 to 1998, due mainly to growth in the use of HFCs.

Emission estimates are presented in this chapter for several industrial processes that are actually accounted for within the Energy chapter. Although CO₂ emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are not the result of the combustion of fossil fuels for energy, their associated emissions are captured in the fuel data for industrial coking coal, natural gas, industrial coking coal, and petroleum coke, respectively. Consequently, if all emissions were attributed to their appropriate chapter, then emissions from energy would decrease by roughly 31 MMTCE in 1998, and industrial process emissions would increase by the same amount.

U.S. Greenhouse Gas Emissions and Sinks: 1990-1998

¹ Carbon dioxide emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are accounted for in the Energy chapter under Fossil Fuel Combustion of industrial coking coal, natural gas, and petroleum coke.

Greenhouse gases are also emitted from a number of industrial processes not addressed in this chapter. For example, caprolactam—a chemical feedstock for the manufacture of nylon 6,6—and urea production are believed to be industrial sources of N_2O emissions. However, emissions for these and other sources have not been estimated at this time due to a lack of information on the emission processes, manufacturing data, or both. As more information becomes available, emission estimates for these processes will be calculated and included in future greenhouse gas emission inventories, although their contribution is expected to be small.²

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), generally involved multiplying production data for each process by an emission factor per unit of production. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically derived emission factors that are biased and, therefore, may not represent U.S. national averages. Additional sources of uncertainty specific to an individual source category are discussed in each section.

Table 3-1 summarizes emissions for the Industrial Processes chapter in units of million metric tons of carbon equivalents (MMTCE), while unweighted gas emissions in Gigagrams (Gg) are provided in Table 3-2.

Table 3-1: Emissions from Industrial Processes (MMTCE)

Table 3-1: Emissions from Industrial Processes Gas/Source	1990	1991	1992	1993	1994	1995	1996	1997	1998
	14.8	14.5	14.6	15.0			17.2	18.0	18.4
CO ₂					16.0	16.8			
Cement Manufacture	9.1	8.9	8.9	9.4	9.8	10.0	10.1	10.5	10.7
Lime Manufacture	3.0	3.0	3.1	3.1	3.2	3.4	3.6	3.7	3.7
Limestone and Dolomite Use	1.4	1.3	1.2	1.1	1.5	1.9	2.0	2.3	2.4
Soda Ash Manufacture and Consumption	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.2	1.2
Carbon Dioxide Consumption	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.4	0.4
Iron and Steel Production*	23.9	19.2	20.7	21.0	21.6	22.2	21.6	21.6	21.9
Ammonia Manufacture*	6.3	6.4	6.7	6.4	6.6	6.5	6.7	6.6	7.3
Ferroalloy Production*	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.5
Aluminum Production*		1.7	1.6	1.5	1.3	1.4	1.4	1.4	1.5
CH_4	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4
Petrochemical Production	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4
Silicon Carbide Production	+	+	+	+	+	+	+	+	+
N_2O	9.9	10.1	9.8	10.2	10.9	11.0	11.3	10.5	7.7
Adipic Acid Production	5.0	5.2	4.8	5.2	5.5	5.5	5.7	4.7	2.0
Nitric Acid Production	4.9	4.9	5.0	5.1	5.3	5.4	5.6	5.8	5.8
HFCs, PFCs, and SF ₆	23.3	22.0	23.5	23.8	25.1	29.0	33.5	35.3	40.3
Substitution of Ozone Depleting Substances	0.3	0.2	0.4	1.4	2.7	7.0	9.9	12.3	14.5
Aluminum Production	5.4	4.7	4.4	3.8	3.2	3.1	3.2	3.0	2.8
HCFC-22 Production	9.5	8.4	9.5	8.7	8.6	7.4	8.5	8.2	10.9
Semiconductor Manufacture	0.8	0.8	0.8	1.0	1.1	1.5	1.9	1.9	2.1
Electrical Transmission and Distribution	5.6	5.9	6.2	6.4	6.7	7.0	7.0	7.0	7.0
Magnesium Production and Processing	1.7	2.0	2.2	2.5	2.7	3.0	3.0	3.0	3.0
Total	48.3	46.9	48.3	49.5	52.3	57.2	62.5	64.2	66.9

⁺ Does not exceed 0.05 MMTCE

^{*} Emissions from these sources are accounted for in the Energy chapter and are not included in the Industrial Processes totals. Note: Totals may not sum due to independent rounding.

² See Annex P for a discussion of emission sources excluded.

Table 3-2: Emissions from Industrial Processes (Gg)

Gas/Source	1990	1991	1992	1993	1994	1995	1996	1997	1998
CO ₂	54,427	53,197	53,512	55,137	58,432	61,735	63,170	66,021	67,447
Cement Manufacture	33,278	32,535	32,792	34,624	36,087	36,847	37,079	38,323	39,227
Lime Manufacture	11,092	10,891	11,245	11,496	11,895	12,624	13,179	13,434	13,627
Limestone and Dolomite Use	5,113	4,896	4,502	4,058	5,541	6,987	7,499	8,537	8,854
Soda Ash Manufacture and	4,144	4,035	4,091	4,048	4,012	4,309	4,273	4,434	4,325
Consumption									
Carbon Dioxide Consumption	800	840	882	912	898	968	1,140	1,294	1,413
Iron and Steel Production ^a	87,600	70,560	75,840	77,120	79,040	81,440	79,040	79,360	80,160
Ammonia Manufacture ^a	23,138	23,364	24,391	23,399	24,316	23,682	24,390	24,346	26,880
Ferroalloy Production ^a	1,809	1,580	1,579	1,516	1,607	1,625	1,695	1,789	1,790
Aluminum Production ^a	5,951	6,058	5,942	5,432	4,850	4,961	5,258	5,296	5,458
CH ₄	57	58	61	67	71	72	76	77	78
Petrochemical Production	56	57	60	66	70	72	75	77	77
Silicon Carbide Production	1	1	1	1	1	1	1	1	1
N_2O	117	119	116	121	129	130	134	124	91
Adipic Acid Production	59	62	57	61	65	66	67	55	23
Nitric Acid Production	58	58	59	60	63	64	67	68	68
HFCs, PFCs, and SF ₆	M	\mathbf{M}	\mathbf{M}	M	M	\mathbf{M}	\mathbf{M}	M	M
Substitution of Ozone Depleting	M	M	M	M	M	M	M	M	M
Substances									
Aluminum Production	M	M	M	M	M	M	M	M	M
HCFC-22 Production ^b	3	3	3	3	3	2	3	3	3
Semiconductor Manufacture	M	M	M	M	M	M	M	M	M
Electrical Transmission and Distribution	on ^c 1	1	1	1	1	1	1	1	1
Magnesium Production and Processing	g ^c +	+	+	+	+	+	+	+	+
Door not avaged 50 Gg									

⁺ Does not exceed 50 Gg

Note: Totals may not sum due to independent rounding.

Cement Manufacture

Cement manufacture is an energy and raw material intensive process resulting in the generation of carbon dioxide (CO_2) from both the energy consumed in making the cement and the chemical process itself.³ Cement production accounts for about 2.4 percent of total global industrial and energy-related CO_2 emissions (IPCC 1996), and the United States is the world's third largest cement producer. Cement is manufactured in almost every state and is used in all of them. Carbon dioxide, emitted from the chemical process of cement production, represents one of the largest sources of industrial CO_2 emissions in the United States.

During the cement production process, calcium carbonate ($CaCO_3$) is heated in a cement kiln at a temperature of about 1,300°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO_2 . This process is known as calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO_2 being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland cement. The production of masonry cement from Portland cement requires additional lime and, thus, results in additional CO_2 emissions. However, this additional lime is

M (Mixture of gases)

^a Emissions from these sources are accounted for in the Energy chapter and are not included in the Industrial Processes totals.

^b HFC-23 emitted

^c SF₆ emitted

 $^{^3}$ The CO_2 emissions related to the consumption of energy for cement manufacture are accounted for under CO_2 from Fossil Fuel Combustion in the Energy chapter.

already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source's total. They are presented here for informational purposes only.

In 1998, U.S. clinker production—including Puerto Rico—totaled 75,859 thousand metric tons, and U.S. masonry cement production reached 3,910 thousand metric tons (USGS 1999). The resulting emissions of CO₂ from clinker production were estimated to be 10.7 MMTCE (39,227 Gg) (see Table 3-3). Emissions from masonry production from clinker raw material were estimated to be 0.02 MMTCE (88 Gg) in 1998, but again are accounted for under Lime Manufacture.

Table 3-3: CO₂ Emissions from Cement Production*

Year	MMTCE	Gg
1990	9.1	33,278
1991	8.9	32,535
1992	8.9	32,792
1993	9.4	34,624
1994	9.8	36,087
1995	10.0	36,847
1996	10.1	37,079
1997	10.5	38,323
1998	10.7	39,227

^{*} Totals exclude CO₂ emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

After falling in 1991 by 2 percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 1998, emissions increased by 18 percent. In 1998, output by cement plants increased 2 percent over 1997, to 75,859 thousand metric tons. Cement is a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, will have considerable influence on cement production in the future. In the near term, a strong domestic economy is a key factor in maintaining high demand for construction materials and, hence, growth in the cement industry and associated CO₂ emissions.

Methodology

Carbon dioxide emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO_2 and lime with the CO_2 released to the atmosphere. The quantity of the CO_2 emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of $CaCO_3$ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO_2 :

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO_2 released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC/UNEP/OECD/IEA 1997) and a constant reflecting the mass of CO_2 released per unit of lime. This yields an emission factor of 0.507 tons of CO_2 per ton of clinker produced. The emission factor was calculated as follows:

$$EF_{Clinker} = 0.646 \ CaO \times \left[\frac{44.01 \ g/mole \ CO_2}{56.08 \ g/mole \ CaO} \right] = 0.507 \ tons \ CO_2/ton \ clinker$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO_2 emissions should be estimated as 2 percent of the CO_2 emissions calculated from clinker production. Total cement

production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC/OECD/IEA 1999).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately 5 percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05/(1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this percentage (2.86 percent) by the molecular weight ratio of CO_2 to CaO (0.785) to yield 0.0224 metric tons of additional CO_2 emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO_2 emissions from the additional lime added during masonry cement production are accounted for in the section on CO_2 emissions from Lime Manufacture. Thus, these emissions were estimated in this chapter for informational purposes only, and are not included in the cement emission totals.

Data Sources

The activity data for clinker and masonry cement production (see Table 3-4) were obtained from U.S. Geological Survey (USGS 1992, 1995, 1996, 1997, 1998, 1999). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants. The 1998 value for masonry cement production was furnished by Hendrick van Oss, USGS.

Table 3-4: Cement Production (Thousand Metric Tons)

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,786	3,283
1995	71,257	3,603
1996	71,706	3,469
1997	74,112	3,634
1998	75,859	3,910

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker, in the amount of lime added to masonry cement, and in the percentage of CKD recycled inside the clinker kiln. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO_2 is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO_2 in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of CO_2 reabsorbed is thought to be minimal, it was not estimated.

Lime Manufacture

Lime, or calcium oxide (CaO),⁴ is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) at coal-fired electric power plants, construction, pulp and paper manufacturing, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States.

Lime production involves three main processes: stone preparation, calcination, and hydration. Carbon dioxide is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO₃)—is roasted at high temperatures in a kiln to produce CaO and CO₂. The CO₂ is driven off as a gas and is normally emitted to the atmosphere. Some of the CO₂ generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)⁵ production. It is also important to note that for certain applications, lime reabsorbs CO₂ during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 20,100 thousand metric tons in 1998 (USGS 1999). This resulted in CO₂ emissions of 3.7 MMTCE (13,627 Gg) (see Table 3-5 and Table 3-6).

Table 3-5: Net CO₂ Emissions from Lime Manufacture

Year	MMTCE
1990	3.0
1991	3.0
1992	3.1
1993	3.1
1994	3.2
1995	3.4
1996	3.6
1997	3.7
1998	3.7

Table 3-6: CO₂ Emissions from Lime Manufacture (Gg)

Year	Potential	Recovered*	Net Emissions
1990	11,574	(483)	11,092
1991	11,454	(563)	10,891
1992	11,843	(598)	11,245
1993	12,261	(765)	11,496
1994	12,699	(804)	11,895
1995	13,502	(878)	12,624
1996	14,013	(834)	13,179
1997	14,378	(944)	13,434
1998	14,670	(1,043)	13,627

^{*} For sugar refining and precipitated calcium carbonate production

Note: Totals may not sum due to independent rounding.

At the turn of the century, over 80 percent of lime consumed in the United States went for construction uses. However, the contemporary lime market is distributed across its four end-use categories as follows: metallurgical uses, 39 percent; environmental uses, 26 percent; chemical and industrial uses, 24 percent, and construction uses, 9 percent. Domestic lime manufacture has increased every year since 1991, when it declined by 1 percent from 1990

⁴ Lime also exists in a dolomitic form (CaO•MgO).

⁵ Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.

levels. Production in 1998 increased 2 percent over the previous year to about 20,100 thousand metric tons. Overall, from 1990 to 1998, lime production, and hence process CO_2 emissions, increased by 23 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993, the U.S. Environmental Protection Agency (EPA) completed regulations under the Clean Air Act capping sulfur dioxide (SO_2) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the FGD end-use to expand from 12 percent of total lime consumption in 1994 to 15 percent in 1998 (USGS 1999).

Methodology

During the calcination stage of lime manufacture, CO_2 is driven off as a gas and normally exits the system with the stack gas. Carbon dioxide emissions were estimated by applying a CO_2 emission factor to the total amount of lime produced. The emission factor used in this analysis is the product of a constant reflecting the mass of CO_2 released per unit of lime and the average calcium plus magnesium oxide (CaO + MgO) content for lime. This yields an emission factor of 0.73 tons of CO_2 per ton of lime produced. The emission factor was calculated as follows:

 $[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.93 \text{ CaO/lime}) = 0.73 \text{ g CO}_2/\text{g lime}$

Lime production in the United States was 20,100 thousand metric tons in 1998 (USGS 1999), resulting in potential CO_2 emissions of 14,670 Gg. Some of the CO_2 generated during the production process, however, was recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. Combined lime manufacture by these producers was 1,785 thousand metric tons in 1998, generating 1.0 Gg of CO_2 . It was assumed that approximately 80 percent of the CO_2 involved in sugar refining and PCC was recovered.

Data Sources

The activity data for lime manufacture and lime consumption by sugar refining and precipitated calcium carbonate (PCC) for 1990 through 1992 (see Table 3-7) were obtained from USGS (1991, 1992); for 1993 through 1994 from Michael Miller (1995); for 1995 through 1998 from USGS (1997, 1998, 1999). The CaO purity of lime was obtained from ASTM (1996) and Schwarzkopf (1995).

Table 3-7: Lime Production and Lime Use for Sugar Refining and PCC (Thousand Metric Tons
--

Year	Production	Use
1990	15,859	826
1991	15,694	964
1992	16,227	1,023
1993	16,800	1,310
1994	17,400	1,377
1995	18,500	1,504
1996	19,200	1,428
1997	19,700	1,616
1998	20,100	1,785

Uncertainty

The term "lime" is actually a general term that includes various chemical and physical forms of this commodity. Uncertainties in the emission estimate can be attributed to slight differences in the chemical composition of these products. For example, although much care is taken to avoid contamination during the production process, lime typically contains trace amounts of impurities such as iron oxide, alumina and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO₂ emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction

applications. In many processes, CO_2 reacts with the lime to create calcium carbonate (e.g., water softening). Carbon dioxide reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate (PCC) reacts with CO_2 ; whereas most of the lime used in steelmaking reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO_2 that is reabsorbed.⁶ As more information becomes available, this emission estimate will be adjusted accordingly.

In some cases, lime is generated from calcium carbonate by-products at paper mills and water treatment plants.⁷ The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the paper industry, mills that employ the sulfate process (i.e., Kraft) consume lime in order to causticize a waste sodium carbonate solution (i.e., black liquor). Most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO_2 —for reuse in the pulping process. However, some of these mills capture the CO_2 released in this process to be used as precipitated calcium carbonate (PCC). Further research is necessary to determine to what extent CO_2 is released to the atmosphere through generation of lime by paper mills.

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

Limestone and Dolomite Use

Limestone (CaCO₃) and dolomite (CaCO₃MgCO₃)⁸ are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process to generate CO_2 as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization (FGD) systems for utility and industrial plants, or as a raw material in glass manufacturing.

In 1998, approximately 17,268 thousand metric tons of limestone and 2,597 thousand metric tons of dolomite were used for these applications. Overall, both limestone and dolomite usage resulted in aggregate CO₂ emissions of 2.4 MMTCE (8,854 Gg) (see Table 3-8 and Table 3-9).

Table 3-8:	CO ₂ Emissions from	om Limestone & Dolomite	Use (MMTCE)
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Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998
Flux Stone	0.8	0.7	0.6	0.5	0.8	1.1	1.2	1.4	1.5
Glass Making	+	+	0.1	0.1	0.1	0.1	0.2	0.2	0.2
FGD	0.5	0.6	0.5	0.5	0.6	0.7	0.7	0.8	0.8

 $^{^6}$ Representatives of the National Lime Association estimate that CO_2 reabsorption that occurs from the use of lime offsets as much as a third of the CO_2 emissions from calcination.

⁷ Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO₂. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) $[CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2]$, not calcium carbonate $[CaCO_3]$. Thus, the calcium hydroxide is heated in the kiln to simply expel the water $[Ca(OH)_2 + heat \rightarrow CaO + H_2O]$ and no CO₂ is released to the atmosphere.

 $^{^8}$ Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Total 1.4 1.3 1.2 1.1 1.5 1.9 2.0 2.3

+ Does not exceed 0.05 MMTCE

Note: Totals may not sum due to independent rounding.

Table 3-9: CO₂ Emissions from Limestone & Dolomite Use (Gg)

Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998
Flux Stone	3,002	2,699	2,314	1,903	2,950	3,903	4,249	5,042	5,327
Limestone	2,550	2,294	1,957	1,597	2,108	2,523	3,330	3,970	4,194
Dolomite	451	406	357	306	842	1,380	919	1,072	1,132
Glass Making	189	170	218	274	356	526	555	593	626
Limestone	189	170	218	274	356	421	445	475	502
Dolomite	NA	NA	NA	NA	NA	105	110	118	124
FGD	1,922	2,027	1,971	1,880	2,235	2,558	2,695	2,902	2,902
Total	5,113	4,896	4,502	4,058	5,541	6,987	7,499	8,537	8,854

NA (Not Available)

Note: Totals may not sum due to independent rounding.

Emissions in 1998 increased 4 percent from the previous year. Although they decreased slightly in 1991, 1992, and 1993, CO₂ emissions from this source have since increased 73 percent from the 1990 baseline. In the future, increases in demand for crushed stone are anticipated. Demand for crushed stone from the transportation sector continues to drive growth in limestone and dolomite use. The Transportation Equity Act for the 21st Century, which commits over \$200 billion dollars to highway work through 2003, promises to maintain the upward trend in consumption.

Methodology

Carbon dioxide emissions were calculated by multiplying the amount of limestone consumed by an average carbon content for limestone, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). Assuming that all of the carbon was released into the atmosphere, the appropriate emission factor was multiplied by the annual level of consumption for flux stone, glass manufacturing, and FGD systems to determine emissions.

Data Sources

Consumption data for 1990 through 1998 of limestone and dolomite used as flux stone and in glass manufacturing (see Table 3-10) were obtained from the USGS (1991, 1993, 1996, 1997, 1998, 1999). Consumption data for limestone used in FGD were taken from unpublished survey data in the Energy Information Administration's Form EIA-767, "Steam Electric Plant Operation and Design Report," (EIA 1997, 1998). For 1990 and 1994, the USGS did not provide a breakdown of limestone and dolomite production by end-use and for 1998 the end-use breakdowns had not yet been finalized at the time of publication. Consumption figures for these years were estimated by assuming that limestone and dolomite accounted for the same percentage of total crushed stone consumption for a given year as the average of the percentages for the years before and after (exception: 1990 and 1998 consumption were estimated using the percentages for only 1991 and 1997, respectively). Furthermore, starting in 1996, USGS discontinued reporting glass manufacture separately. From 1996 onward, limestone used in glass manufacture is estimated based on its percent of total crushed stone for 1995.

It should be noted that there is a large quantity of crushed stone reported to the USGS under the category "unspecified uses". A portion of this consumption is believed to be limestone or dolomite used as flux stone and for

glass manufacture. The quantity listed for "unspecified uses" was, therefore, allocated to each reported end-use according to each end-uses fraction of total consumption in that year.

Table 3-10: Limestone & Dolomite Consumption (Thousand Metric Tons)

Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998
Flux Stone									
Limestone	5,797	5,213	4,447	3,631	4,792	5,734	7,569	9,024	9,533
Dolomite	932	838	738	632	1,739	2,852	1,899	2,215	2,340
Glass Making									
Limestone	430	386	495	622	809	958	1,011	1,079	1,140
Dolomite	NA	NA	NA	NA	NA	216	228	243	257
FGD	4,369	4,606	4,479	4,274	5,080	5,815	6,125	6,595	6,595

NA (Not Available)

Uncertainty

Uncertainties in this estimate are due in part, to variations in the chemical composition of limestone. In addition to calcite, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured. Uncertainties also exist in the activity data. Much of the limestone consumed in the United States is reported as "other unspecified uses"; therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Furthermore, some of the limestone reported as "limestone" is believed to actually be dolomite, which has a higher carbon content than limestone.

Soda Ash Manufacture and Consumption

Soda ash (sodium carbonate, Na_2CO_3) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is the largest soda ash-producing country in the world. Trona is the principal ore from which natural soda ash is made.

Only two states produce natural soda ash: Wyoming and California. Of these two states, only Wyoming has net emissions of CO_2 . This difference is a result of the production processes employed in each state. During the production process used in Wyoming, natural sources of sodium carbonate are heated and transformed into a crude soda ash that requires further refining. Carbon dioxide (CO_2) is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO_2 may also be released when soda ash is consumed.

In 1998, CO₂ emissions from the manufacture of soda ash from trona were approximately 0.4 MMTCE (1,600 Gg). Soda ash consumption in the United States also generated 0.7 MMTCE (2,700 Gg) of CO₂ in 1998. Total emissions

⁹ This approach was recommended by USGS.

 $^{^{10}}$ In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO_2 in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO_2 is generated as a by-product, the CO_2 is recovered and recycled for use in the carbonation stage and is never actually released.

from this source in 1998 were then 1.2 MMTCE (4,325 Gg) (see Table 3-11 and Table 3-12). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 1998 decreased by 2 percent from the previous year, but have increased 4 percent since 1990.

Table 3-11: CO₂ Emissions from Soda Ash Manufacture and Consumption

Year	MMTCE
1990	1.1
1991	1.1
1992	1.1
1993	1.1
1994	1.1
1995	1.2
1996	1.2
1997	1.2
1998	1.2

Table 3-12: CO₂ Emissions from Soda Ash Manufacture and Consumption (Gg)

Year	Manufacture	Consumption	Total
1990	1,435	2,709	4,144
1991	1,429	2,605	4,035
1992	1,451	2,639	4,091
1993	1,412	2,635	4,048
1994	1,422	2,590	4,012
1995	1,607	2,702	4,309
1996	1,587	2,685	4,273
1997	1,666	2,768	4,434
1998	1,607	2,718	4,325

Note: Totals may not sum due to independent rounding.

The United States has the world's largest deposits of trona and represents about one-third of total world soda ash output. The distribution of soda ash by end-use in 1998 was glass making, 49 percent; chemical production, 27 percent; soap and detergent manufacturing, 11 percent; distributors, 5 percent; flue gas desulfurization, 3 percent; pulp and paper production, 2 percent; and water treatment and miscellaneous combined for the remaining 3 percent (USGS 1999).

Soda ash production and consumption decreased by 3.5 and 1.8 percent from 1997 values, respectively. Exports are a driving force behind U.S. soda ash production and the Asian economic crisis beginning in late 1997 has been cited as a major cause for the drop in world soda ash demand. Moderate growth (between 1.5 and 2 percent) is expected for 1999 as the Asian economy recovers and as demand in South America continues to grow (USGS 1999).

Construction is currently underway on a major soda ash plant that will use a new feedstock—nahcolite, a natural sodium bicarbonate found in deposits in Colorado's Piceance Creek Basin. By 2001, the plant is expected to be mining more than 1.4 million tons of nahcolite per year and converting it into 1 million tons of soda ash (C&EN, 1999). Part of this process involves the stripping of CO₂. At this point, it is unknown whether any CO₂ will be released to the atmosphere or captured and used for conversion back to sodium bicarbonate.

Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. Carbon dioxide and water are generated as by-products of the calcination process. Carbon dioxide emissions from the calcination of trona can be estimated based on the following chemical reaction:

$$2(Na_3H(CO_3)_2 \cdot 2H_2O) \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$
 [trona] [soda ash]

Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO_2 . Thus, the 16.5 million metric tons of trona mined in 1998 for soda ash production (USGS 1999) resulted in CO_2 emissions of approximately 0.4 MMTCE (1,600 Gg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO_2 is usually emitted. In these applications, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO_2) are released for every metric ton of soda ash consumed.

Data Sources

The activity data for trona production and soda ash consumption (see Table 3-13) were taken from USGS (1993, 1994, 1995, 1998, and 1999). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry. All six of the soda ash manufacturing operations in the United States completed surveys to provide data to the USGS.

Table 3-13: Soda Ash Manufacture and Consumption (Thousand Metric Tons)

Year	Manufacture*	Consumption
1990	14,734	6,527
1991	14,674	6,278
1992	14,900	6,360
1993	14,500	6,350
1994	14,600	6,240
1995	16,500	6,510
1996	16,300	6,470
1997	17,100	6,670
1998	16,500	6,550

^{*} Soda ash manufactured from trona ore only.

Uncertainty

Emissions from soda ash manufacture are considered to be relatively certain. Both the emissions factor and activity data are reliable. However, emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, uncertainty exists as to the accuracy of the emission factors.

Carbon Dioxide Consumption

Carbon dioxide (CO₂) is used for a variety of applications, including food processing, chemical production, carbonated beverages, and enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the ground to increase reservoir pressure, and is therefore considered sequestered.¹¹ For the most part, however, CO₂ used in non-EOR applications will eventually enter the atmosphere.

 $^{^{11}}$ It is unclear to what extent the CO_2 used for EOR will be re-released. For example, the CO_2 used for EOR may show up at the wellhead after a few years of injection (Hangebrauk et al. 1992). This CO_2 , however, is typically recovered and re-injected into

Carbon dioxide is produced from a small number of natural wells, as a by-product from the production of chemicals (e.g., ammonia), or separated from crude oil and natural gas. Depending on the raw materials that are used, the by-product CO₂ generated during these production processes may already be accounted for in the CO₂ emission estimates from fossil fuel consumption (either during combustion or from non-fuel uses). For example, ammonia is primarily manufactured using natural gas as a feedstock. Carbon dioxide emissions from this process are accounted for in the Energy chapter under Fossil Fuel Combustion and, therefore, are not included here.

In 1998, CO₂ emissions from this source not accounted for elsewhere were 0.4 MMTCE (1,413 Gg) (see Table 3-14). This amount represents an increase of 9 percent from the previous year and is 77 percent higher than emissions in 1990.

Table 3-14: CO₂ Emissions from Carbon Dioxide Consumption

Year	MMTCE	Gg
1990	0.2	800
1991	0.2	840
1992	0.2	882
1993	0.2	912
1994	0.2	898
1995	0.3	968
1996	0.3	1,140
1997	0.4	1,294
1998	0.4	1,413

Methodology

Carbon dioxide emission estimates were based on CO_2 consumption with the assumption that the end-use applications, except enhanced oil recovery, eventually release 100 percent of the CO_2 into the atmosphere. Carbon dioxide consumption for uses other than enhanced oil recovery was about 7,067 thousand metric tons in 1998. The Freedonia Group estimates that, in the United States, there is an 80 to 20 percent split between CO_2 produced as a by-product and CO_2 produced from natural wells. Thus, emissions are equal to 20 percent of CO_2 consumption. The remaining 80 percent was assumed to already be accounted for in the CO_2 emission estimates from other categories (the most important being Fossil Fuel Combustion).

Data Sources

Carbon dioxide consumption data (see Table 3-15) were obtained from *Industrial Gases to 2003*, published by the Freedonia Group Inc. (1994, 1996, 1999). The 1999 report contains actual data for 1998 only. Data for 1996 were obtained by personal communication with Paul Ita of the Freedonia Group Inc. (1997). Data for 1997 production was calculated from annualized growth rates for 1994 through 1996 while the 1997 value for enhanced oil recovery was set equal to the 1998 value. The percent of carbon dioxide produced from natural wells was obtained from Freedonia Group Inc. (1991).

Table 3-15: Carbon Dioxide Consumption

Year	Thousand Metric Tons
1990	4,000
1991	4,200
1992	4,410
1993	4,559

the well. More research is required to determine the amount of CO_2 that in fact escapes from EOR operations. For the purposes of this analysis, it is assumed that all of the CO_2 remains sequestered.

1994	4,488
1995	4,842
1996	5,702
1997	6,468
1998	7,067

Uncertainty

Uncertainty exists in the assumed allocation of carbon dioxide produced from fossil fuel by-products (80 percent) and carbon dioxide produced from wells (20 percent). In addition, it is possible that CO₂ recovery exists in particular end-use sectors. Contact with several organizations did not provide any information regarding recovery. More research is required to determine the quantity, if any, that may be recovered.

Iron and Steel Production

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO_2 . Iron is produced by first reducing iron oxide (ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron of about 4 to 4.5 percent carbon by weight). Carbon dioxide is produced as the coke used in this process is oxidized. Steel (less than 2 percent carbon by weight) is produced from pig iron in a variety of specialized steel furnaces. The majority of CO_2 emissions come from the production of iron, with smaller amounts evolving from the removal of carbon from pig iron to produce steel.

Emissions of CO₂ from iron and steel production in 1998 were 21.9 MMTCE (80,200 Gg). Emissions fluctuated significantly from 1990 to 1998 due to changes in domestic economic conditions and changes in imports and exports. Forecasts for iron and steel production remain mixed. Despite a 5 percent increase in capital expenditures during 1998, plant capacity utilization sank below 80 percent and steel imports continued to climb.

 CO_2 emissions from iron and steel production are not included in totals for the Industrial Processes chapter because they are accounted for with Fossil Fuel Combustion emissions from industrial coking coal in the Energy chapter. ¹² Emissions estimates are presented here for informational purposes only (see Table 3-16). Additional CO_2 emissions also occur from the use of limestone or dolomite flux during production; however, these emissions are accounted for under Limestone and Dolomite Use.

Table 3-16: CO₂ Emissions from Iron and Steel Production

Year		Gg
1990	23.9	87,600
1991	19.2	70,560
1992	20.7	75,840
1993	21.0	77,120
1994	21.6	79,040
1995	22.2	81,440
1996	21.6	79,040
1997	21.6	79,360
1998	21.9	80,160

¹² Although the CO₂ emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Methodology

Carbon dioxide emissions were calculated by multiplying annual estimates of pig iron production by the ratio of CO₂ emitted per unit of iron produced (1.6 metric ton CO₂/metric ton iron). The emission factor employed was applied to both pig iron production and integrated pig iron plus steel production; therefore, emissions were estimated using total U.S. pig iron production for all uses including making steel.

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1997 (see Table 3-17) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Volume I-Metals and Minerals* (USGS 1996, 1997, 1998); data for 1998 were obtained from USGS's *Mineral Commodity Summaries* (1999).

Table 3-17: Pig Iron Production

Year	Thousand Metric Tons
1990	54,750
1991	44,100
1992	47,400
1993	48,200
1994	49,400
1995	50,900
1996	49,400
1997	49,600
1998	50,100

Uncertainty

The emission factor employed was assumed to be applicable to both pig iron production and integrated pig iron plus steel production. This assumption was made because the uncertainty in the factor is greater than the additional emissions generated when steel is produced from pig iron. Using plant-specific emission factors could yield a more accurate estimate, but these factors were not available. The most accurate alternative would be to calculate emissions based on the amount of reducing agent used, rather than on the amount of iron or steel produced; however, these data were also not available.

Ammonia Manufacture

Emissions of CO_2 occur during the production of ammonia. In the United States, roughly 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas, and the remainder is produced using naphtha (a petroleum fraction) or the electrolysis of brine at chlorine plants (EPA 1997). The former two fossil fuel-based reactions produce carbon monoxide and hydrogen gas; however, the latter reaction does not lead to CO_2 emissions. Carbon monoxide (CO) in the first two processes is transformed into CO_2 in the presence of a catalyst (usually a metallic oxide). The hydrogen gas is diverted and combined with nitrogen gas to produce ammonia. The CO_2 , included in a gas stream with other process impurities, is absorbed by a scrubber solution. In regenerating the scrubber solution, CO_2 is released.

$$CH_4 + H_2O \rightarrow 4H_2 + CO_2$$

$$3H_2 + N_2 \rightarrow 2NH_3$$

Emissions of CO₂ from ammonia production in 1998 were 7.3 MMTCE (26,900 Gg). Carbon dioxide emissions from this source are not included in totals for the Industrial Processes chapter because these emissions are accounted

for with non-energy use of natural gas under Fossil Fuel Combustion in the Energy chapter. Emissions estimates are presented here for informational purposes only (see Table 3-18).

Table 3-18: CO₂ Emissions from Ammonia Manufacture

Year	MMTCE	Gg
1990	6.3	23,138
1991	6.4	23,364
1992	6.7	24,391
1993	6.4	23,399
1994	6.6	24,316
1995	6.5	23,682
1996	6.7	24,390
1997	6.6	24,346
1998	7.3	26,880

Methodology

Emissions of CO_2 were calculated by multiplying annual estimates of ammonia production by an emission factor (1.5 ton CO_2 /ton ammonia). It was assumed that all ammonia was produced using catalytic steam reformation, although small amounts may have been produced using chlorine brines. The actual amount produced using this latter method is not known, but assumed to be small.

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Ammonia production data (see Table 3-19) were obtained from the Census Bureau of the U.S. Department of Commerce (Census Bureau 1998, 1999) as reported in *Chemical and Engineering News*, "Facts & Figures for the Chemical Industry."

Table 3-19: Ammonia Manufacture

Year	Thousand Metric Tons
1990	15,425
1991	15,576
1992	16,261
1993	15,599
1994	16,211
1995	15,788
1996	16,260
1997	16,231
1998	17,920

Uncertainty

It is uncertain how accurately the emission factor used represents an average across all ammonia plants. By using natural gas consumption data for each ammonia plant, more accurate estimates could be calculated. However, these consumption data are often considered confidential and are difficult to acquire. All ammonia production in this

 $^{^{13}}$ Although the CO_2 emissions from the use of natural gas as a feedstock should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

analysis was assumed to be from the same process; however, actual emissions could differ because processes other than catalytic steam reformation may have been used.

Ferroalloy Production

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements often including silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (50 and 75 percent silicon) and silicon metal (about 98 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials. As a result, government information disclosure rules prevent the publication of production data for them. Similar to emissions from the production of iron and steel, CO_2 is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced. The CO is eventually oxidized, becoming CO_2 . A representative reaction equation for the production of 50 percent ferrosilicon is given below:

$$Fe_2O_3 + 2SiO_2 + 7C \rightarrow 2FeSi + 7CO$$

Emissions of CO₂ from ferroalloy production in 1998 were 0.5 MMTCE (1,800 Gg). Carbon dioxide emissions from this source are not included in the totals for the Industrial Processes chapter because these emissions are accounted for in the calculations for industrial coking coal under Fossil Fuel Combustion in the Energy chapter.¹⁴ Emission estimates are presented here for informational purposes only (see Table 3-20).

Table 3-20: CO₂ Emissions from Ferroalloy Production

Year	MMTCE	Gg
1990	0.5	1,809
1991	0.4	1,580
1992	0.4	1,579
1993	0.4	1,516
1994	0.4	1,607
1995	0.4	1,625
1996	0.5	1,695
1997	0.5	1,789
1998	0.5	1,790

Methodology

Emissions of CO_2 were calculated by multiplying annual estimates of ferroalloy production by material-specific emission factors. Emission factors were applied to production data for ferrosilicon 50 and 75 percent (2.35 and 3.9 metric ton CO_2 /metric ton, respectively) and silicon metal (4.3 metric ton CO_2 /metric ton). It was assumed that all ferroalloy production was produced using coking coal, although some ferroalloys may have been produced with wood, other biomass, or graphite carbon inputs.

¹⁴ Although the CO₂ emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Data Sources

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Ferroalloy production data for 1990 through 1997 (see Table 3-21) were obtained from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Volume I—Metals and Minerals* (USGS, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998); data for 1998 were obtained from USGS (1999) *Mineral Industry Surveys: Silicon in December 1998*.

Table 3-21: Production of Ferroalloys (Metric Tons)

Year	Ferrosilicon 50%	Ferrosilicon 75%	Silicon Metal
1990	321,385	109,566	145,744
1991	230,019	101,549	149,570
1992	238,562	79,976	164,326
1993	199,275	94,437	158,000
1994	198,000	112,000	164,000
1995	181,000	128,000	163,000
1996	182,000	132,000	175,000
1997	175,000	147,000	187,000
1998	166,000	144,000	195,000

Uncertainty

Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood would not be counted under this source because wood-based carbon is of biogenic origin. Emissions from ferroalloys produced with graphite inputs would be counted in national totals, but may generate differing amounts of CO₂ per unit of ferroalloy produced compared to the use of coking coal. As with emissions from iron and steel production, the most accurate method for these estimates would be basing calculations on the amount of reducing agent used in the process, rather than on the amount of ferroalloys produced. These data were not available, however.

Petrochemical Production

Small amounts of methane (CH₄) are released during the production of some petrochemicals. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. Emissions are presented here from the production of five chemicals: carbon black, ethylene, ethylene dichloride, styrene, and methanol.

Carbon black is an intensely black powder made by the incomplete combustion of an aromatic petroleum feedstock. Almost all output is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Styrene is a common precursor for many plastics, rubber, and resins. It can be found in many construction products, such as foam insulation, vinyl flooring, and epoxy adhesives. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers. The United States produces close to one quarter of the world's supply of methanol.

 $^{^{15}}$ Emissions and sinks of biogenic carbon are accounted for in the Land-Use Change and Forestry chapter.

Aggregate emissions of CH₄ from petrochemical production in 1998 were 0.4 MMTCE (77 Gg) (see Table 3-22). Production levels of all five chemicals increased from 1990 to 1998. Petrochemicals are currently in oversupply and production for 1999 and 2000 is expected to decrease.

Table 3-22: CH₄ Emissions from Petrochemical Production

Year	MMTCE	Gg
1990	0.3	56
1991	0.3	57
1992	0.3	60
1993	0.4	66
1994	0.4	70
1995	0.4	72
1996	0.4	75
1997	0.4	77
1998	0.4	77

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of chemical production by an emission factor. The following factors were used: 11 kg CH_4 /metric ton carbon black, 1 kg CH_4 /metric ton ethylene, 0.4 kg CH_4 /metric ton ethylene dichloride 16 , 4 kg CH_4 /metric ton styrene, and 2 kg CH_4 /metric ton methanol. These emission factors were based upon measured material balances. Although the production of other chemicals may also result in methane emissions, there were not sufficient data to estimate their emissions.

Data Sources

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data (see Table 3-23) were obtained from the Chemical Manufacturers Association *Statistical Handbook* (CMA 1999).

Table 3-23: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990	1991	1992	1993	1994	1995	1996	1997	1998
Carbon Black	1,306	1,225	1,365	1,452	1,492	1,524	1,560	1,588	1,610
Ethylene	16,542	18,124	18,563	18,709	20,201	21,199	22,197	23,088	23,474
Ethylene Dichloride	6,282	6,221	6,872	8,141	8,482	7,829	8,596	9,152	8,868
Styrene	3,637	3,681	4,082	4,565	5,112	5,167	5,387	5,171	5,183
Methanol	3,785	3,948	3,666	4,782	4,904	4,888	5,330	5,806	5,693

Uncertainty

The emission factors used here were based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emissions estimates, however, such data were not available. There may also be other significant sources of methane arising from petrochemical production activities that have not been included in these estimates.

 $^{^{16}}$ The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be dichloroethylene ($C_2H_2Cl_2$) instead of ethylene dichloride ($C_2H_4Cl_2$).

Silicon Carbide Production

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO₂) is reacted with carbon in the form of petroleum coke. Methane is produced during this reaction from volatile compounds in the petroleum coke. Although CO_2 is also emitted from this production process, the requisite data were unavailable for these calculations. Regardless, they are already accounted for under CO_2 from Fossil Fuel Combustion in the Energy chapter. Emissions of CH_4 from silicon carbide production in 1998 (see Table 3-24) were 1 Gg (less than 0.05 MMTCE).

Table 3-24: CH₄ Emissions from Silicon Carbide Production

Year	MMTCE	Gg
1990	+	1
1991	+	1
1992	+	1
1993	+	1
1994	+	1
1995	+	1
1996	+	1
1997	+	1
1998	+	1

⁺ Does not exceed 0.05 MMTCE

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of silicon carbide production by an emission factor (11.6 kg CH_4 /metric ton silicon carbide). This emission factor was derived empirically from measurements taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1998 (see Table 3-25) were obtained from the *Minerals Yearbook: Volume I-Metals and Minerals, Manufactured Abrasives* (USGS, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999).

Table 3-25: Production of Silicon Carbide

Year	Metric Tons
1990	105,000
1991	78,900
1992	84,300
1993	74,900
1994	84,700
1995	75,400
1996	73,600
1997	68,200
1998	69,800

Uncertainty

The emission factor used here was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. A better alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. These data were not available, however.

Adipic Acid Production

Adipic acid production has been identified as an anthropogenic source of nitrous oxide (N_2O) emissions. Worldwide, there are few adipic acid plants. The United States is the major producer with three companies in four locations accounting for approximately one-half of world production. Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Ninety percent of all adipic acid produced in the United States is used in the production of nylon 6,6. It is also used to provide some foods with a "tangy" flavor.

Adipic acid is produced through a two-stage process during which N_2O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone / cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. Nitrous oxide is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream. Process emissions from the production of adipic acid will vary with the types of technologies and level of emissions controls employed by a facility. In 1990, two of the three major adipic acid producing plants implemented N_2O abatement technologies and as of 1998, all of the major adipic acid production facilities had control systems in place. Only one small plant does not control for N_2O , representing approximately 3 percent of production.

Adipic acid production for 1998 was 866 thousand metric tons. Nitrous oxide emissions from this source were estimated to be 2.0 MMTCE (23 Gg) in 1998 (see Table 3-26).

Table 3-26: N₂O Emissions from Adipic Acid Production

Year	MMTCE	Gg
1990	5.0	59
1991	5.2	62
1992	4.8	57
1993	5.2	61
1994	5.5	65
1995	5.5	66
1996	5.7	67
1997	4.7	55
1998	2.0	23

In 1998, adipic acid production reached its highest level in fourteen years. This increase is chiefly due to rising demand for engineering plastics. Though production continues to increase, emissions have been significantly reduced due to the widespread installation of pollution control measures. By 1998, all of the three major producing plants had voluntarily implemented N_2O abatement technology, which resulted in an overall reduction of emissions by approximately 60 percent.

Methodology

Nitrous oxide emissions were calculated by multiplying adipic acid production by the ratio of N_2O emitted per unit of adipic acid produced and adjusting for the actual percentage of N_2O released as a result of plant-specific emission controls. Because emissions of N_2O in the United States are not regulated, emissions have not been well characterized. However, on the basis of experiments (Thiemens and Trogler 1991), the overall reaction stoichiometry for N_2O production in the preparation of adipic acid was estimated at approximately 0.3 kg of N_2O per kilogram of product. Emissions are determined using the following equation:

 $^{^{17}}$ During 1997, the N_2 O emission controls installed by the third plant operated for approximately a quarter of the year.

 N_2O emissions = [production of adipic acid] x [0.3 kg N_2O / kg adipic acid]

x [$1 - (N_2O \text{ destruction factor * abatement system utility factor)}]$

The " N_2O destruction factor" represents the amount of N_2O expressed as a percentage of N_2O emissions that are destroyed by the currently installed abatement technology. The "abatement system utility factor" represents the percent of time that the abatement equipment operates. Overall in the U.S., 63 percent of production employs catalytic destruction, 34 percent uses thermal destruction, and 3 percent of production has no N_2O abatement measures. The N_2O abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer 1999a, 1999b). The abatement system utility factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer 1999a, 1999b).

Data Sources

Adipic acid production data for 1990 through 1995 (see Table 3-27) were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995, 1996). For 1996 and 1997 data were projected from the 1995 manufactured total based upon suggestions from industry contacts. For 1998, production data were obtained from *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999). The emission factor was taken from Thiemens, M.H. and W.C. Trogler (1991). Adipic acid plant capacities for 1998 were updated using *Chemical Week*, Product focus: adipic acid/adiponitrile (CW 1999). Plant capacities for previous years were obtained from *Chemical Market Reporter* (1998).

Table 3-27: Adipic Acid Production

Year	Thousand Metric Tons
1990	735
1991	771
1992	708
1993	765
1994	815
1995	816
1996	835
1997	860
1998	866

Uncertainty

Because N_2O emissions are controlled in some adipic acid production facilities, the amount of N_2O that is actually released will depend on the level of controls in place at a specific production plant. Thus, in order to calculate accurate emission estimates, it is necessary to have production data on a plant-specific basis. In most cases, however, these data are confidential. As a result, plant-specific production figures were estimated by allocating total adipic acid production using existing plant capacities. This creates a degree of uncertainty in the adipic acid production data used to derive the emission estimates as it is necessary to assume that all plants operate at equivalent utilization levels.

The emission factor was based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for N_2O production in the preparation of adipic acid. However, the extent to which the lab results are representative of actual industrial emission rates is not known.

Nitric Acid Production

Nitric acid (HNO₃) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric

acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N_2O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and NO_2 i.e., NO_x . As such the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NOx, NSCR systems are also very affective at destroying N_2O . However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Currently, it is estimated that approximately 20 percent of nitric acid plants use NSCR (Choe, et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce N_2O .

Nitric acid production was 8,504 thousand metric tons in 1998 (C&EN 1999). Nitrous oxide emissions from this source were estimated at 5.8 MMTCE (68 Gg) (see Table 3-28). Nitric acid production for 1998 decreased 1 percent from the previous year, but has increased 18 percent since 1990.

Table 3-28: N₂O Emissions from Nitric Acid Production

Year	MMTCE	Gg
1990	4.9	58
1991	4.9	58
1992	5.0	59
1993	5.1	60
1994	5.3	63
1995	5.4	64
1996	5.6	67
1997	5.8	68
1998	5.8	68

Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N_2O emitted per unit of nitric acid produced. An emissions factor of 8 kg N_2O / tonne HNO₃ was used and represents a combined factor comprising of 2 kg for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg for plants not equipped with NSCR (Reimer & Slaten 1992). An estimated 20 percent of HNO₃ plants in the U.S. were equipped with NSCR (Choe, et al. 1993). In the process of destroying NO_x , NSCR systems also destroy 80 to 90 percent of the N_2O . Hence, the emission factor is equal to $(9.5 \times 0.80) + (2 \times 0.20) = 8$ kg N_2O / mt HNO₃.

Data Sources

Nitric acid production data for 1990 through 1998 (see Table 3-29) were obtained from *Chemical and Engineering News*, "Facts and Figures" (C&EN 1999). The emission factor range was taken from Reimer, R.A., Parrett, R.A., and Slaten, C.S. (1992).

Table 3-29: Nitric Acid Production

Year	Thousand Metric Tons
1990	7,196
1991	7,191
1992	7,381
1993	7,488
1994	7,905
1995	8,020
1996	8,351
1997	8,557
1998	8,504

Uncertainty

In general, the nitric acid industry is not well categorized. A significant degree of uncertainty exists in nitric acid production figures because nitric acid plants are often part of larger production facilities, such as fertilizer or explosive manufacturing. As a result, only a small volume of nitric acid is sold on the market making production figures difficult to track. Emission factors are also difficult to determine because of the large number of plants using many different technologies. Based on expert judgment, it is estimated that the N_2O destruction factor for NSCR nitric acid facilities is associated with an uncertainty of approximately \pm 10 percent.

Substitution of Ozone Depleting Substances

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used primarily as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990¹⁸. Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, unlike ODSs, are not harmful to the stratospheric ozone layer, they are powerful greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 3-30 and Table 3-31.

Table 3-30: Emissions of HFCs and PFCs from ODS Substitution (MMTCE)

Gas	1990	1991	1992	1993	1994	1995	1996	1997	1998
HFC-23	+	+	+	+	+	+	+	+	+
HFC-125	+	+	0.2	0.4	0.2	0.4	0.5	0.6	0.8
HFC-134a	0.2	0.2	0.2	1.0	2.3	5.2	6.9	8.5	9.8
HFC-143a	+	+	+	+	0.1	0.1	0.2	0.4	0.5
HFC-236fa	+	+	+	+	+	+	+	+	0.3
HFC-4310mee	+	+	+	+	0.2	0.3	0.5	0.5	0.5
C_4F_{10}	+	+	+	+	+	+	+	+	+
C_6F_{14}	+	+	+	+	+	+	+	+	+
Others*	0.1	+	+	+	+	0.9	1.8	2.2	2.6
Total	0.3	0.2	0.4	1.4	2.7	7.0	9.9	12.3	14.5

⁺ Does not exceed 0.05 MMTCE

Note: Totals may not sum due to independent rounding.

Table 3-31: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	1991	1992	1993	1994	1995	1996	1997	1998
HFC-23	+	+	+	+	+	2	5	9	15
HFC-125	+	+	236	481	295	459	637	828	1,027
HFC-134a	564	564	626	2,885	6,408	14,596	19,350	24,065	27,693
HFC-143a	+	+	+	12	63	132	234	358	506
HFC-236fa	+	+	+	+	+	+	+	18	148
HFC-4310mee	+	+	+	+	464	946	1,447	1,476	1,505
C_4F_{10}	+	+	+	+	+	+	+	+	+
C_6F_{14}	+	+	+	+	+	+	+	+	+

¹⁸ [42 U.S.C § 7671, CAA § 601]

^{*} Others include HFC-152a, HFC-227ea, and PFC/PFPEs, which are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C_6F_{14} .

Others*	M	M	M	M	M	M	M	M	M
Others	141	141	141	141	141	141	141	141	141

M (Mixture of Gases)

- + Does not exceed 0.5 Mg
- * Others include HFC-152a, HFC-227ea, and PFC/PFPEs, which are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air conditioners and in refrigerant blends such as R-404¹⁹. In 1993, use of HFCs in foams and aerosols began, and in 1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes increased dramatically, from small amounts in 1990, to 14.5 MMTCE in 1998. This increase was the result of efforts to phase-out CFCs and other ODSs in the United States. This trend is expected to continue for many years, and will accelerate in the early part of the next century as HCFCs, which are interim substitutes in many applications, are themselves phased out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*.

Methodology and Data Sources

The EPA used a detailed vintaging model of ODS-containing equipment and products to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual "vintages" of new equipment that enter service in each end-use. This vintaging model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 40 different end-uses, the model produces estimates of annual use and emissions of each compound.

The major end-use categories defined in the vintaging model to characterize ODS use in the United States were: refrigeration and air conditioning, aerosols, solvent cleaning, fire extinguishing equipment, sterilization, and foams.

The vintaging model estimates HFC and PFC use and emissions resulting from their use as replacements for ODSs by undertaking the following steps:

Step 1: Estimate ODS Use in the United States Prior to Phase-out Regulations

The model begins by estimating CFC, halon, methyl chloroform, and carbon tetrachloride use prior to the restrictions on the production of these compounds in the United States. For modeling purposes, total ODS use was divided into more than 40 separate end-uses. The methodology used to estimate baseline ODS use varied depending on the end-use under consideration. The next section describes the methodology used for estimating baseline ODS use in the refrigeration, air conditioning, and fire extinguishing (halon) end-uses. The subsequent section details the methodology used for all other end-uses.

Step 1.1: Estimate Baseline ODS Use for Refrigeration, Air Conditioning, and Fire Extinguishing

¹⁹ R-404 contains HFC-125, HFC-143a, and HFC-134a.

For each equipment type, the model estimates the total stock of ODS-containing equipment during the period 1985 to 1997. The key data required to develop stock estimates for each end-use were as follows:

- Total stock of ODS-containing equipment in use in the United States in 1985
- The annual rate of growth in equipment consumption in each end-use
- The retirement function for equipment in each end-use

Historical production and consumption data were collected for each equipment type to develop estimates of total equipment stock in 1985. For some end-uses, the only data available were estimates of ODS usage. In these cases, the total 1985 stock was estimated by dividing total ODS use by the average charge of ODS in a typical piece of equipment.

Stocks of ODS-containing equipment change over time. In the vintaging model, the growth in equipment stocks in each end-use was simulated after 1985 using growth rates that define the total number of pieces of new equipment added to the stock each year. The model also uses a retirement function to calculate the length of time each piece of equipment is expected to remain in service. These retirement functions are a critical part of the vintaging model because they determine the speed at which the stock of equipment turns over and is replaced by new equipment. In this analysis, point estimates of the average lifetime of equipment in each end-use were used to develop retirement functions. These retirement functions assume 100 percent survival of equipment up to this average age and zero percent survival thereafter.

Given these data, the total equipment stock in service in a given year t was estimated as the equipment stock in the year (t-1), plus new equipment added to the stock in year t, minus retirements in year t.

Annual ODS use was then estimated for each equipment type during the period 1985 through 1998. Because control technologies can reduce particular kinds of ODS use, use estimates were broken down by type of use (e.g., use in new equipment at manufacture and use required to maintain existing equipment). Baseline estimates of ODS use were based on the following data collected for each equipment type:

ODS charge size (the number of kilograms of ODS installed in new equipment during manufacture)
ODS required to maintain existing equipment (In many end-uses, chemical must be regularly added to equipment to replace chemical emitted from the equipment. Such emissions result from normal leakage and from loss during servicing of the equipment.)

With these data, ODS usage for each refrigeration, air conditioning, and fire extinguishing end-use was calculated using the following equation:

(Total stock of existing equipment in use) \times (ODS required to maintain each unit of existing equipment) + (New equipment additions) \times (ODS charge size)

Step 1.2: Estimate Baseline ODS Use in Foams, Solvents, Sterilization, and Aerosol End-Uses

For end-uses other than refrigeration, air conditioning, and fire extinguishing, a simpler approach was used because these end-uses do not require partial re-filling of existing equipment each year. Instead, such equipment either does not require any ODS after initial production (e.g., foams and aerosols), or requires complete re-filling or remanufacturing of the equipment each year (e.g., solvents and sterilants). ODS use does not need to be differentiated between new and existing equipment for these end-uses. Thus, it is not necessary to track the stocks of new and existing equipment separately over time.

The approach used for these end-uses was to estimate total ODS use in 1985 based on available industry data. Future ODS use was estimated using growth rates that predict ODS consumption growth in these end-uses over time, based upon input from industry.

Step 2: Specification and Implementation of Control Technologies

Having established a baseline for ODS equipment in 1985, the vintaging model next defines controls that may be undertaken for purposes of reducing ODS use and emissions within each end-use. The following controls were implemented in the model:

- Replacement of ODS used in the manufacturing of new equipment or in the operation of existing equipment (i.e., retrofits) with alternative chemicals, such as HFCs and PFCs
- Replacement of ODS-based processes or products with alternative processes or products (e.g., the use of aqueous cleaning to replace solvent cleaning with CFC-113)
- Modification of the operation and servicing of equipment to reduce use and emission rates through the application of engineering and recycling controls

Assumptions addressing these types of controls in each end-use were used to develop "substitution scenarios" that simulate the phase-out of ODSs in the United States by end-use. These scenarios represent the EPA's best estimates of the use of control technologies towards the phase-out ODS in the United States, and are periodically reviewed by industry experts.

In addition to the chemical substitution scenarios, the model also assumes that a portion of ODS substitutes are recycled during servicing and retirement of the equipment. Recycling is assumed to occur in the refrigeration and air conditioning and fire extinguishing end-uses.

The substitution scenarios defined for each equipment type were applied to the relevant equipment stocks. The equipment life-cycle was then simulated after the imposition of controls. Substitute chemical use and emissions—including HFCs and PFCs—were calculated for each scenario using the methods described below.

Step 3: Estimate ODS Substitute Use and Emissions (HFCs and PFCs)

ODS substitute use (i.e., HFC and PFC use) was calculated using the same routine described above for refrigeration, air conditioning, and fire extinguishing equipment. In terms of chemical usage, a key question was whether implementation of a given ODS substitute in an end-use changed the quantity of chemical required to manufacture new equipment or service existing equipment. In this analysis, it was assumed that the use of ODS alternatives in new equipment—including HFCs and PFCs—did not change the total charge of initial chemical used in the equipment in each end-use. For certain refrigeration and air conditioning end-uses, however, it was assumed that new equipment manufactured with HFCs and PFCs would have lower leak rates than older equipment. Existing ODS-containing equipment that was retrofitted with HFCs or PFCs was assumed to have a higher leak rate than new HFC/PFC equipment.

The use of HFCs and PFCs in all other end-uses was calculated by simply replacing ODS use with the chemical alternatives defined in the substitution scenarios. The use of HFCs and PFCs was not assumed to change the quantity of chemical used in new or existing equipment for these end-uses.

The vintaging model estimates HFC and PFC emissions over the lifetime of equipment in each end-use. Emissions may occur at the following points in the lifetime of the equipment:

- Emissions upon manufacture of equipment
- Annual emissions from equipment (due to normal leakage, and if applicable, servicing of equipment)
- Emissions upon retirement of equipment

The emissions that occur upon manufacture of refrigeration and air conditioning equipment were assumed to be less than 0.1 percent. Annual emissions of HFCs and PFCs from equipment—due to normal leakage and servicing—were assumed to be constant each year over the life of the equipment. The quantity of emissions at disposal is a function of the prevalence of recycling at disposal.

Emissions for open cell foam were assumed to be 100 percent in the year of manufacture. Closed cell foams were assumed to emit a portion of total HFC/PFC use upon manufacture, a portion at a constant rate over the lifetime of the foam, and the rest at disposal. There were no foam recycling technologies in use in the United States; therefore, HFCs and PFCs remaining in closed cell foam were assumed to be emitted by the end of the product lifetime.

Emissions were assumed to occur at manufacture, during normal operation, and upon retirement of fire extinguishing systems. Emissions at manufacture were assumed to be negligible and emissions upon disposal were assumed to be minimal because of the use of recovery technologies.

For solvent applications, 15 percent of the chemical used in equipment was assumed to be emitted in that year. The remainder of the used solvent was assumed to be reused or disposed without being released to the atmosphere.

For sterilization applications, all chemicals that were used in the equipment were assumed to be emitted in that year.

All HFCs and PFCs used in aerosols were assumed to be emitted in the same year. No technologies were known to exist that recycle or recover aerosols.

Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the EPA vintaging model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the EPA's model is more comprehensive than the IPCC methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

Aluminum Production

Aluminum is a light-weight, malleable, and corrosion resistant metal that is used in many manufactured products including aircraft, automobiles, bicycles, and kitchen utensils. The United States was the largest producer of primary aluminum, with 17 percent of the world total in 1998 (USGS 1999). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in emissions of several greenhouse gases including carbon dioxide (CO_2) and two perfluorocarbons (PFCs): perfluoromethane (CF_4) and perfluoroethane (C_2F_6).

Occasionally, sulfur hexafluoride (SF_6) is also used by the aluminum industry as a fluxing and degassing agent in experimental and specialized casting operations. In these cases it is normally mixed with argon, nitrogen, and/or chlorine and blown through molten aluminum; however, this practice is not used by primary aluminum production firms in the United States and is not believed to be extensively used by secondary casting firms. Where it does occur, the concentration of SF_6 in the mixture is small and a portion of the SF_6 is decomposed in the process (Waite and Bernard 1990, Corns 1990). It has been estimated that 230 Mg of SF_6 were used by the aluminum industry in the United States and Canada (Maiss and Brenninkmeijer 1998); however, this estimate is highly uncertain. Emissions of SF_6 have not been estimated for this source.

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al_2O_3) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na_3AlF_6). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, some of this carbon is oxidized and released to the atmosphere as CO_2 .

Process emissions of CO_2 from aluminum production were estimated at 1.5 MMTCE (5,500 Gg) in 1998 (see Table 3-32). The CO_2 emissions from this source, however, are accounted for under the non-energy use portion of CO_2 from Fossil Fuel Combustion of petroleum coke and tar pitch in the Energy chapter. Thus, to avoid double counting, CO_2 emissions from aluminum production are not included in totals for the Industrial Processes chapter. They are provided here for informational purposes only.

In addition to CO₂ emissions, the aluminum production industry was also the largest source of PFC emissions in the United States. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical

levels required for electrolysis, rapid voltage increases occur, termed "anode effects." These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF_4 and C_2F_6 . In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. The more frequent and long-lasting the anode effects, the greater the emissions.

Primary aluminum production-related emissions of PFCs are estimated to have declined 48 percent since 1990 to 2.5 MMTCE of CF_4 (1.42 Gg) and 0.3 MMTCE of C_2F_6 (0.12 Gg) in 1998, as shown in Table 3-33 and Table 3-34. This decline was both due to reductions in domestic aluminum production and actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects. The EPA supports aluminum smelters with these efforts through the Voluntary Aluminum Industrial Partnership (VAIP).

Table 3-32: CO₂ Emissions from Aluminum Production

Year	MMTCE	Gg
1990	1.6	5,951
1991	1.7	6,058
1992	1.6	5,942
1993	1.5	5,432
1994	1.3	4,850
1995	1.4	4,961
1996	1.4	5,258
1997	1.4	5,296
1998	1.5	5,458

Table 3-33: PFC Emissions from Aluminum Production (MMTCE)

Year	$\mathbf{CF_4}$	C_2F_6	Total
1990	4.7	0.7	5.4
1991	4.1	0.6	4.7
1992	3.9	0.6	4.4
1993	3.3	0.4	3.8
1994	2.8	0.4	3.2
1995	2.8	0.4	3.1
1996	2.8	0.4	3.2
1997	2.6	0.3	3.0
1998	2.5	0.3	2.8

Note: Totals may not sum due to independent rounding.

Table 3-34: PFC Emissions from Aluminum Production (Gg)

Year	CF ₄	C_2F_6
1990	2.67	0.28
1991	2.32	0.24
1992	2.18	0.23
1993	1.88	0.18
1994	1.57	0.15
1995	1.57	0.14
1996	1.60	0.14
1997	1.49	0.13
1998	1.42	0.12

U.S. primary aluminum production for 1998 – totaling 3,713 thousand metric tons – increased slightly from 1997. This increase can be attributed to the reintroduction of previously idled production capacity (USGS 1999). In general, U.S. primary aluminum production is very responsive to imports, mainly from Russia and other republics of

the Former Soviet Union. For example, in 1994 these countries exported 60 percent more ingots (metal cast for easy transformation) to the United States than in 1993, leading to a significant decline in domestic production. However, 1998 imports from Russia were 10 percent below their peak level in 1994 (USGS 1999).

The transportation industry remained the largest domestic consumer of aluminum, accounting for about 29 percent (USGS 1998). Leading automakers have announced new automotive designs that will expand the use of aluminum materials in the near future. The U.S. Geological Survey believes that demand for and production of aluminum will continue to increase.

Methodology

Carbon dioxide is generated during alumina reduction to aluminum metal following the reaction below:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

The CO_2 emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. During alumina reduction, approximately 1.5 to 2.2 metric tons of CO_2 are emitted for each metric ton of aluminum produced (Abrahamson 1992). Based upon the mass balance for a "typical" aluminum smelter (Drexel University Project Team 1996), the emission factor was set at 1.5 metric tons CO_2 per metric ton of aluminum smelted. This value is at the low end of the Abrahamson (1992) range.

The CO₂ emissions from this source are already accounted for under CO₂ Emissions from Fossil Fuel Combustion in the Energy chapter.²⁰ Thus, to avoid double counting, CO₂ emissions from aluminum production are not included in totals for the Industrial Processes chapter.

PFC emissions from aluminum production were estimated using a per unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

PFC (CF₄ or C_2F_6) kg/ton Al = S \times Anode Effect Minutes/Cell-Day

where:

S = Slope coefficient

Anode Effect Minutes/Cell-Day = Anode Effect Frequency X Anode Effect Duration

The slope coefficient was established for each smelter based on actual field measurements, where available, or default coefficients by technology-type based on field measurements. Once established, the slope coefficient was used along with smelter anode effect data, collected by aluminum companies and reported to the VAIP, to estimate emissions factors over time. Emissions factors were multiplied by annual production to estimate annual emissions at the smelter level. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by the IPCC (IPCC/UNEP/OECD/IEA 1997).

 $^{^{20}}$ Although the carbon contained in the anode is considered a non-energy use of petroleum coke or tar pitch and the $^{CO}_2$ emissions it generates should be included in the Industrial Processes chapter, information to distinguish individual non-energy uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Data Sources

Primary aluminum production data for 1990 through 1997 (see Table 3-35) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998). The data for 1998 were taken from *Mineral Industry Surveys: Aluminum in January 1999* (USGS 1999). The USGS requested data from the 13 domestic producers, all of whom responded. The CO₂ emission factor range was taken from Abrahamson (1992). The mass balance for a "typical" aluminum smelter was taken from Drexel University Project Team (1996).

PFC emission estimates were provided by the EPA's Climate Protection Division in cooperation with participants in the Voluntary Aluminum Industrial Partnership (VAIP) program.

Table 3-35: Production of Primary Aluminum

Year	Thousand Metric Tons
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577
1997	3,603
1998	3,713

Uncertainty

Uncertainty exists as to the most accurate CO_2 emission factor for aluminum production. Emissions vary depending on the specific technology used by each plant. However, evidence suggests that there is little variation in CO_2 emissions from plants utilizing similar technologies (IPCC/UNEP/OECD/IEA 1997). A less uncertain method would be to calculate emissions based upon the amount of carbon—in the form of petroleum coke or tar pitch—consumed by the process; however, this type of information was not available.

For PFC emission estimates, the uncertainty in the aluminum production data is relatively low (\pm 1 to 2 percent) compared to the uncertainty in the emissions factors (\pm 10 to 50 percent). Uncertainty in the emissions factors arises from the lack of comprehensive data for both the slope coefficients and anode effect data. Currently, insufficient measurement data exist to quantify a relationship between PFC emissions and anode effect minutes for all smelters. Future inventories will incorporate additional data reported by aluminum companies and ongoing research into PFC emissions from aluminum production.

Emissions of SF_6 from aluminum fluxing and degassing have not been estimated. Uncertainties exist as to the quantity of SF_6 used by the aluminum industry and its rate of destruction as it is blown through molten aluminum.

HCFC-22 Production

Trifluoromethane (HFC-23 or CHF₃) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Since 1990, production and use of HCFC-22 has increased significantly as it has replaced chlorofluorocarbons (CFCs) in many applications. Because HCFC-22 depletes stratospheric ozone,

HCFC-22 production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.²¹ Feedstock production, in contrast, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl₃) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl₅. The reaction of the catalyst and HF produces SbCl_xF_y, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl₂F), HCFC-22 (CHClF₂), HFC-23 (CHF₃), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, or may be captured for use in a limited number of applications.

Emissions of HFC-23 in 1998 were estimated to be 10.9 MMTCE (3.4 Gg), which represents a 15 percent increase in emissions since 1990 (see Table 3-36). This increase is attributable to the 30 percent increase in HCFC-22 production that occurred since 1990; one third of this increase occurred between 1997 and 1998. Separately, the intensity of HFC-23 emissions (the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured) has declined significantly since 1990.

In the future, production of HCFC-22 in the United States is expected to decline as non-feedstock HCFCs production is phased-out. In contrast, feedstock production is anticipated to continue growing steadily, mainly for manufacturing Teflon[®] and other chemical products. All U.S. producers of HCFC-22 are participating in a voluntary program with the EPA to reduce HFC-23 emissions.

Table 3-36: HFC-23 Emissions from HCFC-22 Production

Year	MMTCE	Gg
1990	9.5	3.0
1991	8.4	2.6
1992	9.5	3.0
1993	8.7	2.7
1994	8.6	2.7
1995	7.4	2.3
1996	8.5	2.7
1997	8.2	2.6
1998	10.9	3.4

Methodology

The EPA studied the conditions of HFC-23 generation, methods for measuring emissions, and technologies for emissions control. This effort was undertaken in cooperation with the manufacturers of HCFC-22.

The methodology employed for estimating emissions was based upon measurements of critical feed components at individual HCFC-22 production plants. Individual producers also measured HFC-23 concentrations in their output stream by gas chromatography. Using measurements of feed components and HFC-23 concentrations in output streams, the amount of HFC-23 generated was estimated. HFC-23 concentrations were determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

²¹ As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

Data Sources

Emission estimates were provided by the EPA's Climate Protection Division in cooperation with the U.S. manufacturers of HCFC-22.

Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. It is estimated that the emissions reported are within 20 percent of the true value. This methodology accounted for the declining intensity of HFC-23 emissions over time. The use of a constant emission factor would not have allowed for such accounting. Earlier emission estimates assumed that HFC-23 emissions were between 2 and 4 percent of HCFC-22 production on a mass ratio basis. By 1996, the rate of HFC-23 generated as a percent of HCFC-22 produced dropped, on average, below 2 percent in the United States.

Semiconductor Manufacture

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and chemical vapor deposition (CVD) processes. The gases most commonly employed are trifluoromethane (HFC-23), perfluoromethane ($C_{1}F_{6}$), nitrogen trifluoride (NF₃), and sulfur hexafluoride (SF₆), although other compounds such as perfluoropropane ($C_{3}F_{8}$) and perfluorocyclobutane ($C_{4}F_{8}$) are also used. The exact combination of compounds is specific to the process employed.

Plasma etching is performed to provide pathways for the electrical conducting material to connect individual circuit components in the silicon, using HFCs, PFCs, SF₆ and other gases in plasma. The etching process creates fluorine atoms that react at the semiconductor surface according to prescribed patterns to selectively remove substrate material. A single semiconductor wafer may require as many as 100 distinct process steps that utilize these gases. Chemical vapor deposition chambers, used for depositing materials that will act as insulators and wires, are cleaned periodically using PFCs and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. However, due to the low destruction efficiency (high dissociation energy) of PFCs, a portion of the gas flowing into the chamber flows unreacted through the chamber and, unless emission abatement technologies are used, this portion is emitted into the atmosphere.

In addition to being directly used in the manufacturing processes, these gases can also be transformed during the process into a different HFC or PFC compound, which is then exhausted into the atmosphere. For example, when either CHF₃ or C_2F_6 is used in cleaning or etching, CF₄ is often generated and emitted as a process by-product.

For 1998, it was estimated that total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were 2.1 MMTCE. Combined emissions of all fluorinated greenhouse gases are presented in Table 3-37 below. The rapid growth of this industry and the increasing complexity of semiconductor products could increase emissions in the future.

Table 3-37: Emissions of Fluorinated Greenhouse Gases from Semiconductor Manufacture

Year	MMTCE*
1990	0.8
1991	0.8
1992	0.8
1993	1.0
1994	1.1
1995	1.5
1996	1.9
1997	1.9
1998	2.1

* Combined radiative forcing effect of all gases

Methodology

Emissions were estimated using two sets of data. For 1990 through 1994, emissions were estimated based on the historical consumption of silicon (square centimeters), the estimated average number of interconnecting layers in the chips produced, and an estimated per-layer emission factor. (The number of layers per chip, and hence the PFC emissions per square centimeter of silicon, increases as the line-width of the chip decreases.) The average number of layers per chip was based on industry estimates of silicon consumption by line-width and of the number of layers per line-width. The per-layer emission factor was based on the total annual emissions reported by the participants in the EPA's PFC Emission Reduction Partnership for the Semiconductor Industry. For the three years for which gas sales data are available (1992 through 1994), the estimates derived using historical silicon consumption are within 10 percent of the estimates derived using gas sales data and average values for emission factors and GWPs.

For 1995 through 1998, emissions were estimated based on total annual emissions reported by participants in the EPA's PFC Emission Reduction Partnership for the Semiconductor Industry. As part of the program, partners estimated their emissions using a range of methods; the partners with relatively high emissions typically multiplied estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from suppliers of PFC-based manufacturing equipment. To estimate total U.S. emissions from semiconductor manufacturing based on reported partner emissions, a per-plant emissions factor was estimated for the partners. This per-plant emission factor was then applied to PFC-using plants operated by semiconductor manufacturers who were not partners, considering the varying characteristics of the plants operated by partners and non-partners (e.g., typical plant size and type of device produced). The resulting estimate of non-partner emissions was added to the emissions reported by the partners to obtain total U.S. emissions.

Data Sources

Aggregate emissions estimates for the semiconductor manufacturers participating in the PFC Emission Reduction Partnership were provided by manufacturers (partners). Estimates of the numbers of plants operated by partners and non-partners, and information on the characteristics of those plants, were derived from the International Fabs on Disk database. Estimates of silicon consumed by line-width from 1990 through 1994 were derived from information from VLSI Research, and the number of layers per line-width was obtained from the Semiconductor Industry Association's 1997 National Technology Roadmap.

Uncertainty

Emission estimates for this source are improving, but are still relatively uncertain. Emissions vary depending upon the total amount of gas used and the tool and process in which the gas is used, but not all semiconductor manufacturers track this information. In addition, the relationship between the emissions from semiconductor manufacturers participating in the PFC Emission Reduction Partnership and total U.S. emissions from semiconductor manufacturing is uncertain.

Electrical Transmission and Distribution

The largest use for sulfur hexafluoride (SF_6), both domestically and internationally, is as an electrical insulator in equipment that transmits and distributes electricity. It has been estimated that 30 percent of the worldwide use of SF_6 is leaked from electrical transmission and distribution equipment (Maiss and Brenninkmeijer 1998). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF₆ can escape from gas-insulated substations and switchgear through seals, especially from older equipment. It can also be released during equipment installation and when equipment is opened for servicing,

which typically occurs every few years. In the past, some utilities vented SF₆ to the atmosphere during servicing; however, it is believed that increased awareness and the relatively high cost of the gas have reduced this practice.

Emissions of SF_6 from electrical transmission and distribution systems were estimated to be 7.0 MMTCE (1.07 Gg) in 1998. This quantity amounts to a 25 percent increase over the estimate for 1990 (see Table 3-38).

Table 3-38: SF₆ Emissions from Electrical Transmission and Distribution

Year	MMTCE	Gg
1990	5.6	0.86
1991	5.9	0.90
1992	6.2	0.95
1993	6.4	0.99
1994	6.7	1.03
1995	7.0	1.07
1996	7.0	1.07
1997	7.0	1.07
1998	7.0	1.07

Methodology

The EPA developed its methodology for estimating SF_6 emissions from electrical transmission and distribution systems in 1994. The method estimates actual emissions of SF_6 using a top-down, or production-based approach. Specifically, emissions were calculated based upon the following factors: 1) the estimated U.S. production capacity for SF_6 , 2) the estimated use of this production capacity, 3) the fraction of U.S. SF_6 production estimated to be sold annually to fill or refill electrical equipment, and 4) the fraction of these sales estimated to replace emitted gas.

Based on information gathered from chemical manufacturers, it was estimated that in 1994 U.S. production capacity for SF_6 was approximately 3,000 metric tons. It was assumed that plants were operating at 90 percent capacity, which was consistent with industry averages and implied that 2,700 metric tons of SF_6 were produced in 1994. It was further assumed that 75 percent of U.S. SF_6 sales were made to electric utilities and electrical transmission and distribution equipment manufacturers. This assumption is consistent with the estimate given in Ko, et al. (1993) that worldwide, 80 percent of SF_6 sales is for electrical transmission and distribution systems. Seventy-five percent of annual U.S. production in 1994 was 2,000 metric tons.

Finally, it was assumed that approximately 50 percent of this production, or 1.0 thousand metric tons, replaced gas emitted into the atmosphere in 1994. This amount is equivalent to 6.7 MMTCE (when rounding is performed at the end of the calculation). EPA's estimate was based on information that emissions rates from this equipment were significant and atmospheric measurements that indicated that most of the SF_6 produced internationally since the 1950s had been released. Emissions from electrical equipment were known to occur from the service and disposal of the equipment and leaks during operation. Leaks from older equipment were reported to release up to 50 percent of the equipment's charge per year, although leaks from newer equipment were reported to release considerably less (e.g., less than 1 percent of the charge per year).

It was assumed that emissions have remained constant at 7 MMTCE since 1995.

Data Sources

Emission estimates were provided by EPA's Climate Protection Division in cooperation with U.S. electric utilities and chemical producers.

Uncertainty

There is currently little verifiable data for estimating SF_6 emissions from electrical transmission and distribution systems. Neither U.S. gas consumption nor emission monitoring data were available when these estimates were

developed. The EPA has recently launched a voluntary program with electrical power systems to reduce emissions of SF_6 from equipment used to transmit and distribute electricity such as high voltage circuit breakers, substations, transformers, and transmission lines. The EPA anticipates that better information on SF_6 emissions from electrical equipment will be provided through its voluntary agreements with electrical utilities that use SF_6 in equipment.

Magnesium Production and Processing

The magnesium metal production and casting industry uses sulfur hexafluoride (SF₆) as a covergas to prevent the violent oxidation of molten magnesium in the presence of air. Small concentrations of SF₆ in combination with carbon dioxide and/or air are blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A minute portion of the SF₆ applied reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and some magnesium fluoride. Little conversion or destruction of SF₆ occurs in the magnesium production or casting processes, and it is currently assumed that all SF₆ is emitted to the atmosphere. SF₆ has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes, sulfur dioxide (SO₂), and boron trifluoride (BF₃), which are toxic and more corrosive at higher concentrations.

For 1998, a total of 3.0 MMTCE (0.5 Gg) of SF_6 was estimated to have been emitted by the magnesium industry, 76 percent more than was estimated for 1990 (see Table 3-39). There are no significant plans for expansion of primary magnesium production in the United States, but demand for magnesium metal for die casting is growing as auto manufacturers design more magnesium parts into vehicle models. The increased demand for primary magnesium is expected to be met by magnesium producers located outside the United States

Table 3-39: SF₆ Emissions from Magnesium Production and Processing

Year	MMTCE	Gg
1990	1.7	0.3
1991	2.0	0.3
1992	2.2	0.3
1993	2.5	0.4
1994	2.7	0.4
1995	3.0	0.5
1996	3.0	0.5
1997	3.0	0.5
1998	3.0	0.5

Methodology

Emissions were estimated from gas usage information supplied to the EPA by primary magnesium producers. Consumption was assumed to equal emissions in the same year. Although not directly employed, the Norwegian Institute for Air Research (NIAR 1993) has reported a range of emission factors for primary magnesium production as being from 1 to 5 kg of SF_6 per metric ton of magnesium. A survey of magnesium die casters has also reported an average emission factor of 4.1 kg of SF_6 per metric ton of magnesium parts die cast (Gjestland and Magers 1996).

Data Sources

Emission estimates were provided by the EPA's Climate Protection Division in cooperation with the U.S. primary magnesium metal producers and casting firms.

Uncertainty

There are a number of uncertainties in these estimates, including the assumption that SF_6 does not react nor decompose during use. It is possible that the melt surface reactions and high temperatures associated with molten magnesium would cause some gas degradation. As is the case for other sources of SF_6 emissions, verifiable SF_6 consumption data for magnesium production and processing in United States were not available. The EPA has recently launched a voluntary partnership with magnesium producers and casters to reduce emissions of SF_6 from

magnesium production and processing. The EPA anticipates that data provided by magnesium firms will improve future SF_6 emission estimates.

Sulfur hexafluoride may also be used as a covergas for the casting of molten aluminum with a high magnesium content; however, it is uncertain to what extent this practice actually occurs.

[BEGIN BOX]

Box 3-1: Potential Emission Estimates of HFCs, PFCs, and SF₆

Emissions of HFCs, PFCs and SF₆ from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are "actual emissions," which are defined by the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 1997) as estimates that take into account the time lag between consumption and emissions. In contrast, "potential emissions" are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Because all chemicals consumed will eventually be emitted into the atmosphere, in the long term the cumulative emission estimates using the two approaches should be equivalent unless the chemical is captured and destroyed. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- By-product emissions. Some emissions do not result from the consumption or use of a chemical, but are the unintended by-products of another process. For such emissions, which include emissions of CF₄ and C₂F₆ from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- Potential emissions that equal actual emissions. For some sources, such as magnesium production and processing, it is assumed that there is no delay between consumption and emission and that no destruction of the chemical takes place. It this case, actual emissions equal potential emissions.
- Emissions that are not easily defined. In some processes, such as semiconductor manufacture, the gases used in the process may be destroyed or transformed into other compounds, which may also be greenhouse gases. It is therefore not logical to estimate potential emissions based on consumption of the original chemical.

Table 3-40 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances and SF_6 emissions from electrical transmission and distribution and other miscellaneous sources such as tennis shoes and sound insulating windows.²² Potential emissions associated with the substitution for ozone depleting substances were calculated through a combination of the EPA's Vintaging Model and information provided by U.S. chemical manufacturers. For other SF_6 sources, estimates were based on an assumed U.S. SF_6 production capacity and plant utilization to estimate total sales. The portion of this amount used for magnesium processing and assumed to be used for semiconductor manufacture were subtracted.

Table 3-40: 1998 Potential and Actual Emissions of HFCs, PFCs, and SF₆ from Selected Sources (MMTCE)

²² See Annex P for a discussion of sources of SF₆ emissions excluded from the actual emissions estimates in this report.

Source	Potential	Actual
Substitution of Ozone Depleting Substances	45.7	40.3
Aluminum Production	-	2.8
HCFC-22 Production	-	10.9
Semiconductor Manufacture	-	2.1
Magnesium Production and Processing	3.0	3.0
Other SF ₆ Sources*	15.0	7.0

⁻ Not applicable.

[END BOX]

Industrial Sources of Criteria Pollutants

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of criteria air pollutants. Total emissions of nitrogen oxides (NO_x), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 1998 are reported in Table 3-41.

Table 3-41: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990	1991	1992	1993	1994	1995	1996	1997	1998
NO _x	921	802	785	774	939	842	979	890	915
Chemical & Allied Product Manufacturing	152	149	148	141	145	144	130	131	133
Metals Processing	88	69	74	75	82	89	69	70	72
Storage and Transport	3	5	4	4	5	5	5	5	5
Other Industrial Processes	343	319	328	336	353	362	343	348	354
Miscellaneous*	335	259	231	219	354	242	433	334	351
CO	9,502	7,088	5,401	5,421	7,708	5,291	7,899	7,432	7,669
Chemical & Allied Product Manufacturing	1,074	1,022	1,009	992	1,063	1,109	668	676	684
Metals Processing	2,395	2,333	2,264	2,301	2,245	2,159	1,383	1,416	1,449
Storage and Transport	69	25	15	46	22	22	72	73	74
Other Industrial Processes	487	497	494	538	544	566	533	546	559
Miscellaneous*	5,479	3,210	1,619	1,544	3,833	1,435	5,242	4,721	4,903
NMVOCs	3,179	2,983	2,811	2,893	3,043	2,859	2,859	3,002	3,066
Chemical & Allied Product Manufacturing	575	644	649	636	627	599	332	332	336
Metals Processing	111	112	113	112	114	113	409	422	435
Storage and Transport	1,356	1,390	1,436	1,451	1,478	1,499	1,193	1,211	1,225
Other Industrial Processes	364	355	376	401	397	409	398	400	409
Miscellaneous*	774	482	238	292	428	240	525	637	662

^{*} Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, TSDFs (Transport, Storage, and Disposal Facilities under the Resource Conservation and Recovery Act), cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Agricultural Residue Burning source.

Note: Totals may not sum due to independent rounding.

Methodology and Data Sources

The emission estimates for this source were taken directly from the EPA's *National Air Pollutant Emissions Trends*, 1900-1998 (EPA 1999). Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

^{*}Includes Electrical Transmission and Distribution and, in the case of potential emissions, other miscellaneous sources.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors*, *AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data.

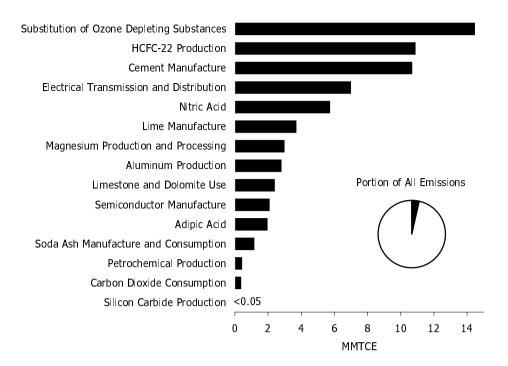


Figure 3-1: 1998 Industrial Processes Chapter GHG Sources